電気材料技術雑誌 第9巻第2号
J.Soc.Elect.Mat.Eng. Vol.9, No.2, 2000

Optical Properties of Periodic Multilayer Structure Based on Poly(*p*-phenylene vinylene)s

T. Fujisawa, T. Sonoda, R. Ootake, A. Fujii and K. Yoshino
Department of Electronic Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan
Tel: +81-6-6879-7759, Fax: +81-6-6879-7774
E-mail: tfujisaw@ele.eng.osaka-u.ac.jp

Conducting polymers with highly extended conjugated π-electron systems in the main chains have attracted great interest from both fundamental and practical viewpoints, because they exhibit various novel properties such as insulator-metal transition upon doping,[1] electroluminescent (EL) devices,[2,3] photovoltaic effect.[4]

A self-assembly method is one of the important techniques to fabricate ultrathin polymer film or polymer multilayer film controlled in molecular level.[5,6] In the self-assembly method, charged substrates are repeatedly dipped in cation and anion solutions alternately and alternating multilayers of the cation and anion are formed by Coulombic force between cation and anion on the substrates. Utilizing various combination of many kinds of cation and anion materials, various self-assembled multilayers utilizing conducting polymers could be fabricated and their applications were demonstrated. Previously, we found efficient photoinduced charge separation at interfaces of self-assembled conducting polymers, and suggested the efficient photocells as one of the applications.[7,8]

Poly(*p*-phenylene vinylene) (PPV) and its derivatives are the most attractive materials for polymer light-emitting diodes (LED) and lasers, because of their high luminescent quantum efficiency. Recently, we have developed a PPV derivative, poly(1,4-(2-(5-carboxypentyloxy)-5-methoxyphenylene)vinylene) (CPMOPPV), for the self-assembly method, and studied its optical and electrical properties.[9] Since this polymer indicates the characteristics of a polyanion, self-assembled alternating multilayer structures based on PPVs could be formed utilizing PPV-precursor as a polycation.[10]

In this paper, we report the optical properties of periodic multiplayer structure based on PPV and CPMOPPV.

Preparation of and PPV-precursor and CPMOPPV were reported previously.[9,10] CPMOPPV is soluble in common organic solvents such as acetone, ethanol and tetrahydrofuran (THF). The sodium salt of CPMOPPV, which is obtained by adding sodium hydroxide (NaOH), is soluble even in

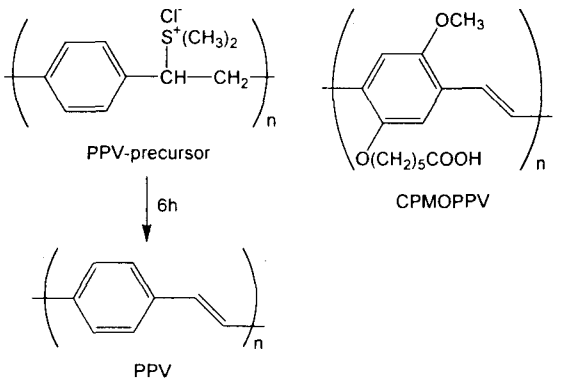

Fig. 1. The molecular structures of PPV-precursor, PPV and CPMOPPV.

water. PPV could be obtained by annealing PPV-precursor at 200 °C for 6 h in vacuum. The molecular structures of PPV-precursor, PPV and CPMOPPV are shown in Fig. 1. CPMOPPV and PPV-precursor were used as a polyanion and a polycation, respectively.

The periodic multilayer structure of these polymers were formed by the self-assembly method on quartz substrates for optical measurements and In-Sn-oxide (ITO)-coated glass substrates with a sheet resistance of 10 Ω/□ for EL measurements. Namely, precleaned quartz or ITO glass substrates were ultrasonicated in acetone for 1 h and immersed into a toluene solution of N-(2-aminoethyl-3- aminopropyl)trimethoxy silane (TMS) of 5 vol% for 15 h. Then, the substrates were heated in toluene at 50 °C for 1 h and washed with toluene, a toluene-methanol mixture (1:1) and methanol to remove the excess TMS. Besides, the substrates were ultrasonicated in distilled water for 10 min and dried at 55 °C in air for 30 min. The substrates were thus coated by TMS monolayer charged positively. The substrates were immersed into a methanol solution of CPMOPPV in concentration of 0.01 M for 15 min in order to form the first adsorbed layer of CPMOPPV. Then, the substrates or fibers were washed extensively with methanol and distilled water in sequence. A PPV-precursor layer was formed by immersing the substrates or fibers into an aqueous solution of PPV-precursor (0.01 M) for 15 min, and then washed with distilled water and methanol in sequence. By repeating the processes, the multilayer structures of CPMOPPV/PPV-precursor were fabricated on the substrates. CPMOPPV/PPV multilayer structures were obtained by thermal conversion of the CPMOPPV/PPV-precursor multilayer structures.

Figure 2 shows the optical absorption spectra of CPMOPPV/PPV multilayers depending on the number of bilayers. The absorption peak around 430 nm is corresponding to the π - π * transition of CPMOPPV and PPV, therefore the conversion from CPMOPPV/PPV-precursor multilayers to CPMOPPV/PPV multilayers was successfully performed, the detailed studies of which were reported elsewhere.[10,11] The absorption spectra of CPMOPPV/PPV multilayers were essentially superposition of those of CPMOPPV and PPV. The inset of Fig. 2 shows the absorbance of CPMOPPV/PPV multilayers at 430 nm depending on the number of bilayers, and the absorption of CPMOPPV/PPV multilayers increased in proportion to the number of bilayers, which indicates that the thickness of each bilayer is almost constant.

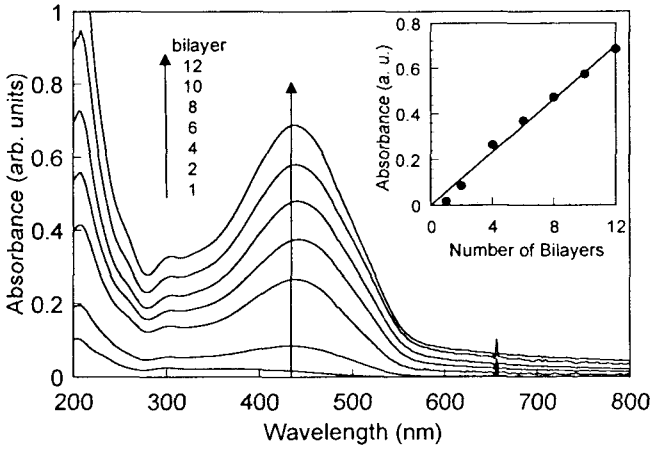

Fig. 2. Absorption spectra of the CPMOPPV/PPV multilayer structures. The inset shows the dependence of the absorbance at 430 nm on the number of bilayers in the CPMOPPV/PPV multilayer structures.

The PL spectra of CPMOPPV/PPV multilayers are shown in Fig. 3, when the 430nm blue light from Xe lamp is adopted as the excitation source. The PL peak around 570 nm is corresponding to the radiative recombination of excitons or exciton polarons in the main chains of CPMOPPV, and slightly red-shifted in comparison with the PL peak of CPMOPPV spin-coated film which is located around 550 nm.[9] The PL intensity of CPMOPPV/PPV multilayers markedly increased with

increasing the number of bilayers without spectral changes. As is apparent in the inset of Fig. 3, the linear relationship was observed between the PL intensity at 570 nm and the number of bilayers. Such results also exhibit that constant amounts of the polymers were adsorbed by the immersion processes, that is, the PL intensity as well as the absorbance shows the relative thickness of the polymers.

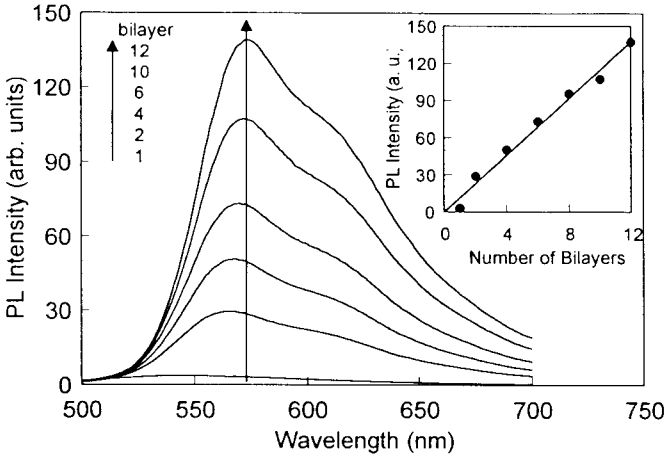

Fig. 3. Photoluminescence spectra of the CPMOPPV/PPV multilayer structures. The inset shows the dependence of the PL intensity at 570 nm on the number of bilayers in the CPMOPPV/PPV multilayer structures.

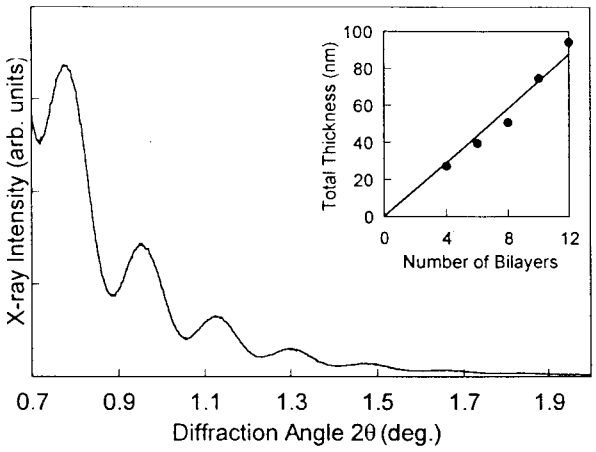

Fig. 4. X-ray diffraction pattern of a 8-bilayer film of CPMOPPV/PPV multilayer structure. The inset shows the dependence of the film thickness on the number of bilayers.

X-ray diffraction pattern of the 8-bilayer film of the CPMOPPV/PPV multilayer was shown in Fig. 4. The several broad peaks were observed in the figure. Such peaks were also observed in CPMOPPV/PPV multilayer with different number of bilayers. The peaks must be attributed to the total thickness of the thin films, which might imply that the film surface is quite smooth. The film thickness could be evaluated from the differential between the peaks and increased linearly depending on the number of bilayers, as shown in the inset of Fig 4. Therefore, the thickness of each bilayer is roughly estimated to be 7 nm.

In the EL diodes with CPMOPPV/PPV multilayers as emission layers, that is, with a structure of ITO/(CPMOPPV/PPV)$_n$/Al, strong yellow EL was observed. The EL diodes exhibited typical rectifying characteristics. The emission intensity starts to increase at around 7 V and increases monotonically with increasing injection current. By applying a positive bias voltage of, for example, +10 V to ITO electrode in the EL diodes with seven bilayers of CPMOPPV/PPV multilayer, a bright yellow emission was obtained, the EL spectrum of which is shown in Fig. 5.

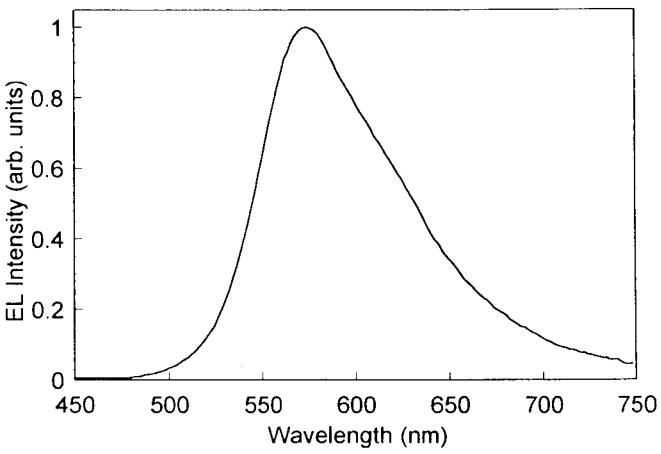

Fig. 5. Electroluminescence spectrum of the LED with seven bilayers of CPMOPPV/PPV multilayer at room temperature in vacuum.

In summary, periodic multilayer structure based on PPVs was fabricated successfully by self-assembly method. Alternative multilayer consisting of CPMOPPV and PPV were adsorbed

onto the positively charged substrates, that was confirmed by the absorption measurement. The optical properties of the periodic multilayer structures of PPVs were also studied and PL efficiency of CPMOPPV was found to be maintained independently of the number of bilayers. EL devices with the structure of ITO/(CPMOPPV/PPV)$_n$/Al were fabricated and strong yellow electroluminescence was observed.

References

[1] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su: Rev. Mod. Phys., **60** (1988) 781.
[2] Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino: Jpn. J. Appl. Phys., **30** (1991) L1938.
[3] Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino: Jpn. J. Appl. Phys., **30** (1991) L1941.
[4] S. Morita, A. A. Zakhidov, and K. Yoshino: Solid State Commun., **82** (1992) 249.
[5] G. Decher, J. D. Hong, and J. Schmitt: Thin Solid Films., **210/211** (1992) 831.
[6] M. Ferreira, J. H. Cheung, and M. F. Rubner: Thin Solid Films., **244** (1994) 806.
[7] T. Kawai, T. Yamaue, K. Tada, M. Onoda, S-H. Jin, S-K. Choi, and K. Yoshino: Jpn. J. Appl. Phys., **35** (1996) L741.
[8] T. Yamaue, T. Kawai, M. Onoda, and K. Yoshino: Jpn. J. Appl. Phys., **38** (1999) 6008.
[9] A. Fujii, T. Sonoda, and K. Yoshino: Jpn. J. Appl. Phys., **39** (2000) L133.
[10] T. Sonoda, A. Fujii, and K. Yoshino: submitted to Jpn. J. Appl. Phys.
[11] T. Sonoda, T.Fujisawa, A. Fujii, and K. Yoshino: submitted to Appl. Phys. Lett.